Table 1. Preventive activity of the stereoisomers of 2-cyano-*N*-[1-(2,4-dichlorophenyl)ethyl]-3,3-dimethylbutyramide.[a]

	Activity[b] at concentration (mg litre^{-1})					
Isomer	6.3	3.1	1.6	0.8	0.4	0.2
(R, R)	3	2	2	1	0	
(S, S)	0					
(R, S)	0					
(S, R)	4	4	4	3	3	1
(RS, R)	4	4	3	3	2	0
(RS, RS)	4	3	3	2	1	0

[a] Pot test with rice blast disease.
[b] 4; >90, 3; 70–89, 2; 50–69, 1; 30–49, 0; <29% control.

configuration at the amine moiety were inactive. The [*(S)*acid, *(R)*amine]-isomer was the most active, both in inhibiting fungal melanin biosynthesis *in vitro* and in pot tests on rice blast disease.

Racemization at the C-2 position of the acid moiety bearing the cyano group proceeds easily under basic conditions. Thus, the compound having the *(RS)*-configuration at the acid and the *(R)*-configuration at the amine moiety and containing enolizable hydrogen at the C-2 position of the acid is being developed as a new rice blasticide (S-2900, proposed common name diclocymet). It should be added that some related amides with an *(S)*-configuration at the amine moiety have been reported to be more herbicidal than bromobutide.[2]

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Synthesis and juvenile hormone activity of benzimidazolylterpenes possessing a 2,7-dimethyloctane skeleton

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Abstract: Benzimidazolylterpenes, possessing a 2,7-dimethyloctane skeleton showed IGR-activity on pupae of *Tenebrio molitor* L in laboratory tests: *N*-(7-methoxy-2,7-dimethyl-2-octenyl)benzimidazole showed the greatest activity.

Keywords: benzimidazolylterpenes; juvenile hormone activity

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1 INTRODUCTION

Most of the insect growth regulators (IGRs) with juvenile hormone (JH) activity known to date are derived from monoterpenes and sesquiterpenes. Several imidazolyl- and benzimidazolyl monoterpene derivatives have shown anti-juvenile hormone activity in larvae of the silk worm, *Bombix mori* L.[1,2] Industrial production of terpene and sesquiterpene derivatives is a very expensive process and this limits the use of IGRs in agricultural practice. We have prepared *N*-monoterpenyl benzimidazoles, having the terpenyl moiety differing from that in natural terpenes in the position of methyl substituents and in the position of the double bond of main chain, i.e with a 2,7-dimethyloctane skeleton (eg **1** Fig 1). Such terpene derivatives can be synthesized by one-pot synthesis from isoprene. We prepared *N*-(2,7-dimethylocta-2,7-dien-1-yl)-benzimidazole (**2**), *N*-(2,7-dimethylocta-1,7-dien-3-yl)benzimidazole (**3**) and *N*-(7-methoxy-2,7-dimethyl-2-octen-1-yl)benzimidazole, (**1**) and tested them for IGR activity.

2 EXPERIMENTAL

2.1 Synthesis

The general procedure was palladium-catalysed allylic alkylation of benzimidazole with a tetra-alkyl ammonium salt (Fig 1; Scheme 1). The chosen salts were *N*-alkyl-*N*-methylpiperidinium iodides. The details of the syntheses of **2** and **3** have been published.[3] Compound **5**, the intermediate for **1**, was prepared as shown in Fig 1, Scheme 2. The alkyl piperidine (**6**) was prepared from isoprene and piperidine by a previously described method[4] and allowed to react with methanol in the presence of acid. The resulting amine (**7**) was converted into the *N*-alkyl-*N*-methylpiperidinium salt (**5**) by reaction with methyl iodide. Allylic alkylation of benzimidazole by **5** was achieved by catalysis with $Pd(dba)_2$. Compound **1** was produced in admixture with 5% of the product of allylic rearrangement.

2.1.1 N-(7-Methoxy-2,7-dimethyl-2-octen-1-yl)piperidine (7)

Perchloric acid (570 g litre^{-1}; 21.6 ml) was added dropwise to solution of amine **6** (7.2 g; 32.5 mmol) in methanol (22 ml) and the mixture was heated under reflux for 14 h. Sodium hydroxide in methanol (150 g litre^{-1}; 50 ml) was then added and the methanol removed under vacuum. The residue was diluted with water, extracted with benzene and the organic phase was dried (sodium sulfate). Removal of the benzene and fractional distillation of the residue gave amine **7** as a colourless oil; yield: 5 g (61%); bp 107–109 °C/

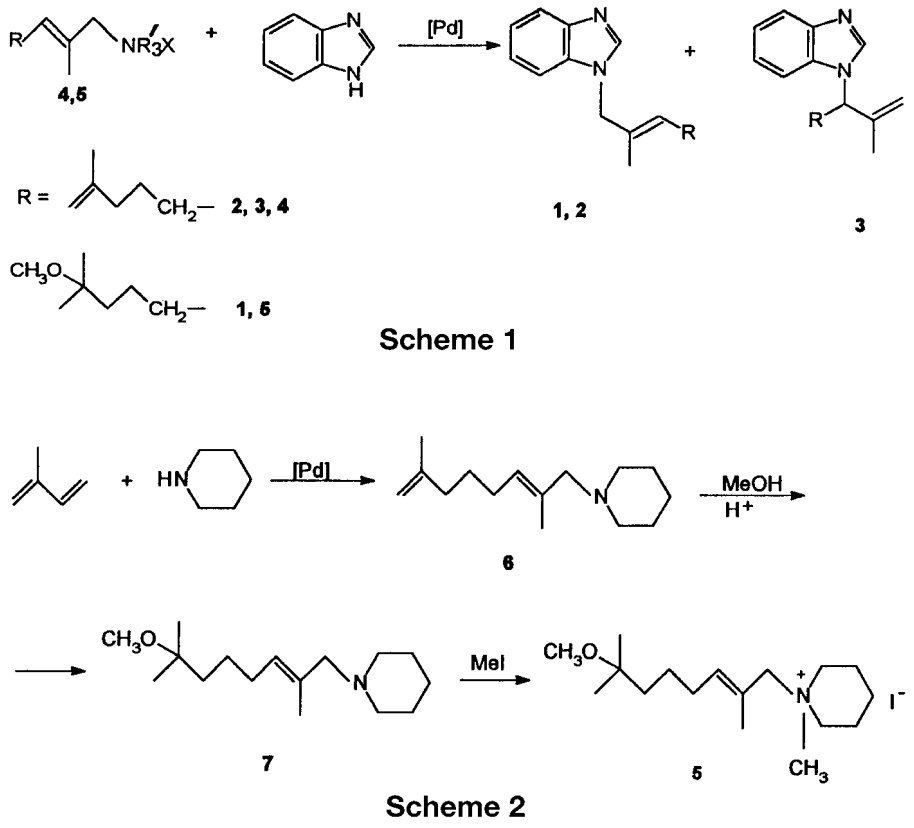

Figure 1. Outline of synthetic methods.

5 Torr. The product had satisfactory C and H analytical values.

2.1.2 N-(7-Methoxy-2,7-dimethyl-2-octen-1-yl)-N-methylpiperidinium iodide (5)

A mixture of compound 7 (3.8 g, 13.4 mmol), methyl iodide (3.8 g, 26.8 mmol) and benzene (3 ml) was kept at 25 °C for 24 h under an argon atmosphere. A light yellow oil precipitated from the solution. The benzene was poured off, hexane (20 ml) was added to the crude yellow oil and the mixture was agitated. The oil was solidified and dried at 1 Torr giving **5** as a white powder; yield: 4.9 g (92%); mp 59–60 °C. The product had satisfactory C, H and N analytical values.

2.1.3 N-(7-Methoxy-2,7-dimethyl-2-octen-1-yl)benzimidazole (1)

Benzimidazole (1.2 g, 9.8 mmol), compound **5** (3.9 g, 9.8 mmol) and $Pd(dba)_2$ (0.28 g, 0.49 mmol, 5 mol%) were dissolved under an argon atmosphere in a mixture of tetrahydrofuran (40 ml) and dimethylformamide (5 ml). Sodium hydride (0.26 g, 10.7 mmol) was added as powder. The homogeneous mixture remaining after evolution of hydrogen had ceased was heated under reflux for 40 h. The solvents were then removed under vacuum, the residue was mixed with hexane and any solid remaining was filtered off. The hexane was then removed under vacuum and the oily residue was distilled to afford **1** as a yellow oil; yield 2.58 g (92%); bp 185 °C/1 Torr.

[^{1}H]NMR ($CDCl_3$/TMS, Varian VXR-400), δ ppm: 1.12 and 1.20 (s, s, 6H, $^{7a}CH_3$, $^{8}CH_3$), 1.38–1.45 (m, 4H, $^{5}CH_2$, $^{6}CH_2$), 1.54 (s, 3H, $^{2a}CH_3$), 3.13 (s, 3H, OCH_3), 4.63 (s, 2H, $^{1}CH_2$), 5.45 (t, 1H, ^{3}CH, J = 7.6 Hz), 7.27 (m, 2H, $^{4'}CH$, $^{5'}CH$), 7.38 (m, 1H, $^{3'}CH$), 7.80 (m, 1H, $^{6'}CH$), 7.88 (s, 1H, $^{2'}CH$). MS, *m/z* (relative intensity): 286 (M^+, 15).

2.2 Testing for juvenile hormone (JH) activity

JH activity of compounds **1–3** was tested on pupae of *Tenebrio molitor* L. from the laboratory's collection at the Research Institute for Plant Protection Chemicals (RIPPC). Insecticidal activity was determined by applying the chemicals (1 μl per pupa of an acetone solution containing 1000 mg litre^{-1} of test compound) topically to the ventral abdominal surface of pupae of *T molitor* within 0–6 h after their emergence. Each compound was tested with 2 × 20 pupae. Treated pupae were kept at 26 °C. The effectiveness of compounds **1–3** was estimated during the period of imago emergence of *T molitor* (after 8–9 days) using Schmialec's scale[5] i.e on a scale 0–9 where 0 signified that treated pupae gave a normal imago and 9 signified when treated pupae did not give a normal imago and did not differ from starting control pupae. The intermediate scores defined a gradation of morphogenetic changes in pupal-imaginal intermediates. We used Altosid- SR-10 (methoprene) as a standard.

3 RESULTS AND DISCUSSION

After estimation of morphological changes of each

Table 1. Biossay results of compounds **1–3** against *Tenebrio molitor* pupae

Run	Compound	Concentration (mg litre^{-1})	N	ΔN	$\Delta N/N$,%
1	**2**	1000	3.1	0.36	11.7
2	**3**	1000	3.5	0.80	22.8
3	**1**	1000	6.0	0.55	9.1
4	Altozid-SR-10	1000	9.0		

individual, the weighted average score (N) for compounds **1**–**3** was determined using the formula:

$$N = \frac{x_1 \cdot 1 + x_2 \cdot 2 + x_3 \cdot 3 + \cdots + x_n \cdot n}{A}$$

The average error (ΔN) was calculated by the formula:

$$\Delta N = \frac{x_1|N-1| + x_2|N-2| + \cdots + x_n|N-n|}{A}$$

1, 2, 3, … n – score from zero to nine,

x_1, x_2, x_3, … x_n – number of individuals with each score,

A – total number of individuals.

The results of bioassays are presented in Table 1.

In contrast to 1,2-, 1,5-, and 1,6-disubstituted benzimidazoles reported by Kuwano,[1] we studied 1-terpenylbenzimidazole without substituents in the 2, 5 or 6 positions of the benzimidazole ring. Furthermore, the structure of the terpenyl moiety differed from that of the natural terpenes by the position of the methyl groups and of the double bond. Benzimidazoles **1**–**3** showed lower insecticidal activity than that of the methoprene standard. The isomer of geranylbenzimidazole, compound **2**, showed poor activity in this series; the activity of the linalylbenzimidazole isomer, compound **3**, was greater. Imagos, resulting from the action of compounds **2** and **3** on pupae, had pupal cuticle on some parts of their bodies. With the introduction of methoxy group in the 7-position of the terpenyl chain the insecticidal activity was expressed; thus the treatment of pupae with compound **1** gave living pupal-imaginal intermediates in which abdomens had pupal cuticle and wing buds were greatly reduced.

4 CONCLUSIONS

It was found that the monoterpenylbenzimidazoles **1**–**3** with 2,7-dimethyloctane skeleton of the terpenyl moiety are insect growth regulators with juvenile hormone activity.

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Photolysis of imidacloprid (NTN 33893) on the leaf surface of tomato plants

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Abstract: The photolytic behaviour of the insecticide imidacloprid on the surface of tomato leaves as a result of exposure to natural sunlight was investigated. Photodegradation in sunlight was rapid and the degradation products (⩾10%) were similar to those found in plant degradation studies.

Keywords: imidacloprid; photodegradation; tomato

An imidacloprid spray solution (0.1 mg ml^{-1}), containing [*methylene*-^{14}C] imidacloprid (Fig 1; sp act 4.64 MBq mg^{-1}), was prepared by adding labelled compound (106 µg; 492.26 kBq), thoroughly mixed with the formulants, to a commercial 200 g litre^{-1} SL formulation, (Confidor® SL 200), diluting with water and thoroughly agitating the mixture in an ultrasonic bath. The identity of the imidacloprid was verified both before and after application.

In practice, tomato leaves are sprayed to run-off with the formulation at 0.1 mg AI ml^{-1}. In the present work, one leaf (area *c* 30 cm^2) of each plant received 10 droplets of the spray solution (total 2.5 µl) which were then distributed over the leaf surface as a thin film, using a rubber-tipped wiper (Fig 2). Measurement of the radioactive content of the applied spray solution and the wiper indicated that each leaf received slightly less than 2.5 µg imidacloprid.

Experiments 1 and 2 were performed outdoors in Monheim, Germany (45 m above NN; 51°4′ latitude North, 6°55′ longitude East) 3 m in front of a greenhouse. The plants were arranged so that the treated leaves faced south. The incident radiation was measured at a point corresponding to the position occupied by the treated leaves, at 300–800 nm (Radialux) in Experiment 1 and 300–400 nm (UV-sensor) in Experiment 2. Experiment 3 (the dark control) was performed in the greenhouse, the treated

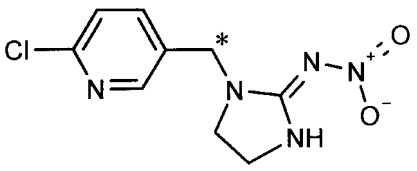

Figure 1. ^{14}C-labelled imidacloprid used in this work; * = labelling position.

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